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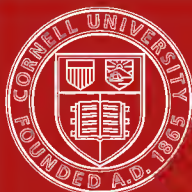
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Brief course in qualitative analysis.



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A BRIEF COURSE
IN
QUALITATIVE ANALYSIS

BY

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NEW YORK
HENRY HOLT AND COMPANY

1898
①

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ROBERT DRUMMOND, PRINTER, NEW YORK.

PREFACE.

It has been the aim in the preparation of this manual to render it as concise as possible with the least sacrifice of a study of reactions and solubilities of chemical importance. For this reason, many of the reactions found in larger books have been omitted.

The following are the points covered in the manual: Preliminary Reactions on Bases and Acids; Schemes of Analysis for Bases and Acids; Brief Explanatory Notes on the Analyses; Treatment of Solid Substances (Powders, Alloys or Metals); Table of Solubilities of salts of the Bases studied. A comprehensive list of questions on Qualitative Analysis, that will force the student *to think*, completes the Manual. These questions, together with the explanatory notes on the schemes of analysis, it is hoped will excite the student's interest and prove a source of inspiration as well as an incentive to intelligent work.

The book is intended merely as a laboratory guide, and should be supplemented by frequent "Quiz Classes" and by constant personal attention. The educational value of such instruction cannot be overestimated.

It is through personal contact with the teacher that the *rationale* of scientific work is understood, and without the requisite amount of this personal instruction Qualitative Analysis becomes mere "test-tubing" and an arbitrary and perfunctory thing, instead of the branch of logical Science which it is.

This Brief Course has been satisfactorily given in the Drexel Institute within the allotted time of one laboratory

period (four hours) and one hour for a lecture or quiz per week, during the school year of thirty-two weeks.

I take pleasure in acknowledging the advice and assistance received from Mr. Abraham Henwood, Instructor in Chemistry in the Drexel Institute, in the preparation of this manual.

E. A. C.

PHILADELPHIA, PA.,

May 1, 1898.

LABORATORY INSTRUCTIONS.

Qualitative Analysis.

Classification of the Metals for Use in Chemical Analysis.

GROUP I.

Silver, lead, mercury (*mercurious*).

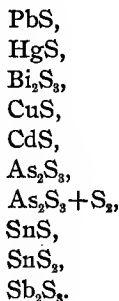
Precipitated by the group reagent, hydrochloric acid, HCl , as:—



GROUP II.

Lead (imperfectly removed by reagent of Group I.), mercury (*mercuric*), bismuth, copper, cadmium, arsenic (*arsenious* and *arsenic*), tin (*stannous* and *stannic*), antimony.

Precipitated by the group reagent, hydrogen sulphide, H_2S , as:—



GROUP III.

Iron (*ferrous* and *ferric*), aluminium, chromium, nickel, cobalt, manganese, zinc.

Precipitated by the group reagent, ammonium sulphide, $(\text{NH}_4)_2\text{S}$, as:—

FeS (from both *ferrous* and *ferric* compounds),

$\text{Al}_2(\text{OH})_6$,

· $\text{Cr}_2(\text{OH})_6$,

NiS ,

CoS ,

MnS ,

ZnS .

GROUP IV.

Barium, strontium, and calcium.

Precipitated by the group reagent, ammonium oxalate, as:—

BaC_2O_4 ,

SrC_2O_4 ,

CaC_2O_4 .

GROUP V.

Magnesium, potassium, sodium (ammonium).

Not precipitated by a group reagent.

A.—Reactions of the Metals.

GROUP I.

SILVER. Ag.

Valence = I.

Use preferably AgNO_3 .

1. HCl precipitates AgCl .

White, curdy, darkens on exposure to light.

Soluble in NH_4OH , KCN .

Insoluble in HNO_3 and other dilute mineral acids; soluble in concentrated HCl .

2. H_2S or alkaline sulphides precipitate Ag_2S .

Black.

Insoluble in alkaline sulphides.

Insoluble in dilute mineral acids.

Soluble in boiling HNO_3 .

3. NH_4OH , NaOH , or KOH precipitates Ag_2O .

Brown.

Insoluble in excess of NaOH or KOH ; soluble in excess of NH_4OH .

Soluble in HNO_3 .

4. KCN precipitates AgCN .

White, curdy.

Soluble in excess of KCN .

Soluble in NH_4OH .

Insoluble in HNO_3 .

5. Heated with the blowpipe on charcoal, + Na_2CO_3 , silver is reduced from all its compounds and forms bright malleable globules which are soluble in HNO_3 .

LEAD. Pb.

Valence = II.

Use preferably $\text{Pb}(\text{NO}_3)_2$.

6. HCl precipitates PbCl_2 .

White, pulverulent.

Insoluble in alcohol.

Decidedly soluble in cold water.

Completely soluble in boiling water.

Soluble in sodium acetate and salts of organic acids.

Soluble in concentrated HCl.

7. H_2S or alkaline sulphides precipitate PbS .

Black. (All lead compounds are blackened by H_2S .)

Insoluble in excess of alkaline sulphides.

Insoluble in quite dilute mineral acids.

Soluble in hot, moderately concentrated HNO_3 .

Converted to PbSO_4 by concentrated HNO_3 .

8. NH_4OH , NaOH , or KOH precipitates $\text{Pb}(\text{OH})_2$.

White.

Insoluble in excess of NH_4OH .

Soluble in excess of NaOH and KOH .

9. KCN precipitates $\text{Pb}(\text{CN})_2$.

White, pulverulent.

Insoluble in excess of KCN .

Soluble in HNO_3 .

10. H_2SO_4 precipitates PbSO_4 .

White, pulverulent.

Insoluble in dilute mineral acids.

Insoluble in alcohol.

Soluble in excess of concentrated H_2SO_4 .

Soluble in alkaline solutions of salts of organic acids, especially acetic and tartaric.

11. K_2CrO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$ precipitates PbCrO_4 .

Yellow.

Soluble in HNO_3 with difficulty.

Soluble in NaOH or KOH .

12. Heated with the blowpipe on charcoal, + Na_2CO_3 , lead is reduced from all its compounds and forms soft, malleable, easily fusible globules which yield a yellow incrustation of PbO .

MERCURY (Mercurous). Hg. Valence = I.

Use preferably $\text{Hg}_2(\text{NO}_3)_2$.

13. HCl precipitates Hg_2Cl_2 .

White, pulverulent.

Converted by NH_4OH into $\text{NH}_2\text{Hg}_2\text{Cl}$, black.

Oxidizing agents convert Hg_2Cl_2 into the soluble chloride, HgCl_2 .

14. NH_4OH precipitates $\text{NH}_2\text{Hg}_2\text{NO}_3$.

Black.

15. NaOH or KOH precipitates Hg_2O .

Black. (Readily decomposes into $\text{HgO} + \text{Hg}$.)

16. SnCl_2 precipitates Hg_2Cl_2 and finally metallic Hg, grey.

17. Heated in a glass tube with dry Na_2CO_3 , mercury is reduced from all its compounds. It is vaporized and condenses in the cooler part of the tube, forming globules.

Scheme of Analysis of Group I.

+ dilute HCl.		
Ppt = AgCl. Treat + hot water.	PbCl ₂ .	Hg ₂ Cl ₂ .
Residue = AgCl, Hg ₂ Cl ₂ . Treat + NH ₄ OH.		Solution PbCl ₂ . Confirm Pb by 7, 10 or 11.
Residue NH ₂ Hg ₂ Cl. Confirm Hg by 17.	Solution NH ₃ AgCl. Confirm Ag by 1.	

Alternative Scheme.

+ HCl, dilute. Filter and treat precipitate.

+ KOH in excess.	
Residue = AgCl. Hg ₂ Cl ₂ or Hg ₂ O.	Solution K ₂ PbO ₂ . Confirm Pb by 7.
Mix + dry Na ₂ CO ₃ . Heat in glass tube to completely expel Hg. Forms mirror. Collect globules of Hg. Dissolve in HNO ₃ . Confirm Hg by 21. Residue Ag ₂ O, NaCl, excess Na ₂ CO ₃ . Treat with hot water. Dissolve residue in dilute HNO ₃ . Confirm by 1.	

Note.—Examine filtrate from precipitation + HCl, for remaining groups.

Notes on Analysis of Group I.

I. Lead is not completely removed in the first group by the reagent HCl , as the PbCl_2 dissolves somewhat in water; hence small amounts of Pb are always found in Group II. if the metal has been found in Group I.

II. The action of NH_4OH after the removal of the Pb is to convert the AgCl and Hg_2Cl_2 into substituted ammonium compounds. The first of these, being soluble, is found in the filtrate, and the second, an insoluble compound, remains as a black residue.

III. Compounds of metals of the first group are reduced with particular ease when heated on charcoal with Na_2CO_3 , giving metallic globules all of which are easily soluble in HNO_3 . (For mercury a glass tube closed at one end is used.)

IV. Note that silver compounds are, as a rule, soluble in NH_4OH but not in NaOH or KOH ; lead compounds are insoluble in NH_4OH but easily soluble in NaOH or KOH ; and mercurous compounds are insoluble in both.

GROUP II.

MERCURY (*Mercuric*). Hg. Valence = II.

Use preferably HgCl_2 .

18. H_2S or alkaline sulphides precipitate finally HgS .
Black.

Insoluble in HNO_3 .

Insoluble in $(\text{NH}_4)_2\text{S}$.

✓ Soluble in Na_2S , K_2S .

✓ Soluble in NaOH , KOH .

✓ Soluble in aqua regia ($\text{HCl} + \text{HNO}_3$) or in other mixtures yielding Cl_2 .

- ✓ 19. NH_4OH precipitates NH_2HgCl .
White (distinction from Mercurous, see 14).
- ✓ 20. KOH or NaOH precipitates finally HgO .
Yellow.
Insoluble in excess of reagent.
21. SnCl_2 precipitates Hg_2Cl_2 and finally metallic Hg .
White at first and finally grey.
22. See 17.

BISMUTH. Bi. Valence = III.

Use preferably BiCl_3 .

23. H_2S or alkaline sulphides precipitate Bi_2S_3 .
Very dark brown.
Insoluble in dilute acids.
Insoluble in alkaline hydroxides.
Insoluble in alkaline sulphides.
Insoluble in KCN .
Soluble in moderately concentrated HNO_3 .
24. NH_4OH , NaOH , KOH precipitates $\text{Bi}(\text{OH})_3$.
White, flocculent.
Insoluble in excess of reagent.
25. H_2O precipitates BiOCl .
White, pulverulent.
Insoluble in tartaric acid (distinction from antimony).
26. K_2SnO_2 in excess, precipitates Bi_2O_2 .
Black.

COPPER. Cu. Valence = II.

Use preferably CuSO_4 .

27. H_2S or soluble sulphides precipitate CuS .
Brownish black.
Insoluble in Na_2S and K_2S .
Insoluble in KOH or NaOH .

Insoluble in dilute acids.

✓ Soluble in HNO_3 .

Very slightly soluble in $(\text{NH}_4)_2\text{S}$.

Soluble in KCN.

Oxidized, when moist, to CuSO_4 by O in the air.

28. NH_4OH precipitates $\text{Cu}(\text{OH})_2$, immediately soluble in excess forming a deep blue solution. $\text{Cu}(\text{NH}_3)_4(\text{OH})_2$

29. KOH or NaOH precipitates $\text{Cu}(\text{OH})_2$.

Light blue.

Insoluble in excess of reagent.

Converted by boiling into CuO , black.

✓ 30. $\text{K}_4\text{Fe}(\text{CN})_6$ precipitates $\text{Cu}_2\text{Fe}(\text{CN})_6$, reddish brown.
add $\text{HC}_2\text{H}_3\text{O}_2$

This forms even in very dilute solutions.

31. Fe or Zn, in neutral or acid solutions, precipitates metallic Cu.

32. Heated with the blowpipe on charcoal + Na_2CO_3 , copper is reduced from all its compounds and forms red malleable grains.

33. Copper compounds color beads of borax or microcosmic salt, blue in the oxidizing flame and opaque red (due to Cu_2O) in the reducing flame.

34. Copper compounds acidified with HCl color the flame blue or green.

CADMIUM. Cd.

Valence = II.

Use preferably CdSO_4 .

35. H_2S or alkaline sulphides precipitate CdS .

Yellow.

Insoluble in dilute HCl.

Insoluble in alkaline sulphides.

Insoluble in NaOH and KOH.

Insoluble in KCN.

Soluble in HNO_3 , and in boiling H_2SO_4 and HCl.

36. NH_4OH precipitates $\text{Cd}(\text{OH})_2$.
 White.
 Soluble in excess of reagent.
37. NaOH or KOH precipitates $\text{Cd}(\text{OH})_2$.
 White.
 Insoluble in excess of reagent.
38. All compounds of Cd when heated on charcoal with
 Na_2CO_3 , give CdO as a brown tarnish which exhibits
 a play of colors.

ARSENIC (Arsenious). As . Valence = III.

Use preferably Na_3AsO_3 .

39. H_2S precipitates from acid solutions, As_2S_3 .
 Yellow.
 Insoluble in concentrated HCl .
 Soluble in concentrated HNO_3 .
 Soluble in alkaline sulphides.
 Soluble in alkaline carbonates and hydroxides.
40. AgNO_3 added to neutral solutions precipitates Ag_3AsO_3 .
 Yellow. (Easily soluble in HNO_3 and in NH_4OH .)
41. Nascent hydrogen acting on arsenic solutions produces
 in all cases AsH_3 gas (*highly poisonous!*) "Marsh
 Test." Inflammable—burns to $\text{As}_2\text{O}_3 + \text{H}_2\text{O}$.
 Arsenic, as a lustrous mirror, is separated if the flame
 be chilled, *e. g.* by the introduction of cold porcelain.
 Dissociated by heat with the separation of metallic
 As . Soluble in HNO_3 ; in NaClO .
 Passed into a solution of AgNO_3 forms H_3AsO_3 . Neu-
 tralized + dilute NH_4OH forms Ag_3AsO_3 . Yellow
 ring.
42. A strip of copper added to solutions of arsenic com-
 pounds acidified with HCl , and heated, becomes

coated with a gray deposit. (Reinsch Test.) On heating this strip in an open tube with free access of air, the white oxide As_2O_3 is formed. Crystalline and easily volatilized.

43. All arsenic compounds heated on charcoal + Na_2CO_3 are reduced to arsenic which volatilizes with a characteristic garlic-like odor.
44. Oxidizing agents, such as HNO_3 , Cl , NaClO , $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{K}_2\text{Mn}_2\text{O}_8$, convert *arsenious* into *arsenic* compounds.

ARSENIC (*Arsenic*). As . Valence = V.

Use preferably Na_3AsO_4 .

45. H_2S reduces *arsenic* compounds to *arsenious* with the separation of S. It then precipitates As_2S_3 .
Yellow.
See 39.
46. Alkaline sulphides precipitate As_2S_5 .
Yellow.
Insoluble in HCl .
Soluble in excess of reagents.
47. MgSO_4 in the presence of NH_4Cl + NH_4OH precipitates $\text{MgNH}_4\text{AsO}_4$.
White, crystalline.
Insoluble in NH_4OH .
Easily soluble in dilute acids.
48. See 41.
49. See 42.
50. See 43.
51. Reducing agents, such as H_2S , SO_2 , convert *arsenic* into *arsenious* compounds.

✓ **TIN (Stannous). Sn. Valence = II.**

Use preferably SnCl_2 .

52. H_2S precipitates SnS .

Brown.

Insoluble in alkaline mono-sulphides.

Insoluble in dilute acids.

✓ Soluble in alkaline poly-sulphides.

✓ Soluble in alkaline hydroxides.

✓ Soluble in concentrated HCl .

53. Alkaline sulphides precipitate SnS .

Brown.

✓ Soluble in excess of the reagent, if poly-sulphides are used.

54. Alkaline hydroxides precipitate $\text{Sn}(\text{OH})_2$.

White.

Insoluble in excess of NH_4OH .

Soluble in excess of NaOH and KOH .

55. HgCl_2 is reduced by stannous salts with the precipitation of Hg_2Cl_2 ; later Hg precipitates.

(See 21. Distinction from stannic compounds.)

56. All tin compounds, when mixed with Na_2CO_3 and KCN and heated on charcoal, are reduced to globules of Sn , with an accompanying white incrustation of SnO_2 .

Moistened with $\text{Co}(\text{NO}_3)_2$ and heated with blowpipe, a bluish green color results.

57. Oxidizing agents, such as HNO_3 , Cl , Fe_2Cl_6 , convert stannous compounds to stannic.

TIN (Stannic). Sn. Valence = IV.

Use preferably SnCl_4 .

58. H_2S precipitates SnS_2 .

Yellow.

Insoluble in dilute acids.





Insoluble in $(\text{NH}_4)_2\text{CO}_3$.

Soluble in concentrated HCl .

✓ Soluble in alkaline sulphides.

Soluble in fixed alkaline hydroxides.

59. Alkaline sulphides precipitate SnS_2 .

Yellow.

✓ Soluble in excess of the reagent.

60. Alkaline hydroxides precipitate $\text{SnO}(\text{OH})_2$.

White.

Insoluble in excess of NH_4OH .

✓ Soluble in excess of KOH and NaOH .

61. Neutral salts of the alkali metals, such as Na_2SO_4 and NH_4NO_3 , give on boiling a precipitate of stannic or meta-stannic acid, H_2SnO_3 , or $(\text{H}_2\text{SnO}_3)_n$.

62. See 56.

63. Reducing agents, such as nascent hydrogen and certain metals (Sn , Cu), convert stannic compounds first to stannous and finally, in some cases, to metallic Sn .

ANTIMONY. Sb .

Valence = III.

Use preferably SbCl_3 .

64. H_2S precipitates Sb_2S_3 .

Orange-red.

Insoluble in dilute acids.

Insoluble in $(\text{NH}_4)_2\text{CO}_3$.

Soluble in alkaline sulphides.

Soluble in alkaline hydroxides.

Soluble in concentrated HCl .

Soluble in hot concentrated $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$.

65. Alkaline sulphides precipitate Sb_2S_3 .

Orange-red.

Soluble in excess of the reagent.

66. Alkaline hydroxides precipitate $\text{Sb}(\text{OH})_3$.
 White.
 Insoluble in excess of NH_4OH .
 Soluble in excess of KOH and NaOH .
67. H_2O causes the precipitation of SbOCl .
 White.
 Easily soluble in $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$. (Distinction from Bi.)
68. Analogous to arsenic. See 41. The gas SbH_3 , passed into a solution of AgNO_3 , precipitates Ag_3Sb . (Distinction from As.)
 Metallic Sb is converted into Sb_2O_3 by means of HNO_3 ; insoluble in NaClO . (Distinctions from As.)
69. Zinc in the presence of HCl and Pt precipitates Sb as a dull black adherent coating on the Pt. Insoluble in HCl . Converted into oxide by HNO_3 .
70. Heated with Na_2CO_3 on charcoal in the reducing flame, brittle beads of Sb are formed. These are easily converted by oxidation into the volatile Sb_2O_3 which coats the coal. Moistened with $\text{Co}(\text{NO}_3)_2$ and ignited, an olive green color is developed.

+ H_2S gas through warm, dilute solution, acid with HCl .
 Precipitate:
 (PbS), HgS , Bi_2S_3 , CuS , CdS , SnS , SnS_2 , As_2S_3 , Sb_2S_3 .
 (Filtrate to be examined for remaining groups.)
 Digest + $(\text{NH}_4)_2\text{S}_x$ warm.

Residue: (PbS) HgS , Bi_2S_3 , CuS , CdS . Treat + hot dilute HNO_3 (1—1).	Filtrate: $\text{Pb}(\text{NO}_3)_2$, $\text{Bi}(\text{NO}_3)_3$, $\text{Cu}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2$, + dilute H_2SO_4 .	Precip.: PbSO_4 . Confirm Pb by 7.	Filtrate: $\text{Bi}_2(\text{SO}_4)_3$, CuSO_4 , CdSO_4 .	+ NH_4OH in excess. Precip.: $\text{Bi}(\text{OH})_3$ Confirm Bi by 26.	Filtrate: NH_4 salts of Cu + Cd . Deep blue if Cu is present. Acidify + HCl . + Clean Iron. Precip.: Cu . Red. Solution: Dilute + H_2O pass H_2S = CdS — yellow. Confirm Cd by 38.
Filtrate. $(\text{NH}_4)_2\text{AsS}_3$, $(\text{NH}_4)_3\text{SbS}_3$, $(\text{NH}_4)_2\text{SnS}_3$, + dilute H_2SO_4 . Precipitate: SnS_2 , Sb_2S_3 , As_2S_3 , + concentrated HCl and boil.	Residue: As_2S_3 . Dissolve in HNO_3 . Confirm As by 47.	Solution: SnCl_4 , SbCl_3 . Dilute + H_2O . Add Zn + Pt . Sb precipitated on Pt . Confirm Sb by 69. Sn precipitated on Zn . Confirm Sn after solution in HCl by 55.			

Alternative Scheme of Analysis.

+ H₂S through warm, dilute solution, acid + HCl.

Precipitate:

(PbS), HgS, Bi₂S₃, CuS, CdS, As₂S₃, Sb₂S₃, SnS, SnS₂.

(Filtrate to be examined for remaining groups.)

Digest + (NH₄)₂S_x warm.

Residue:		Filtrate:	
(PbS), HgS, Bi ₂ S ₃ , CuS, CdS. Treat + dilute HNO ₃ (1-1).		(NH ₄) ₂ AsS ₃ , (NH ₄) ₂ SbS ₃ , (NH ₄) ₂ SnS ₃ + dilute H ₂ SO ₄ . As ₂ S ₃ , SnS ₂ , Sb ₂ S ₃ . Boil + excess saturated solution H ₂ C ₂ O ₄ .	
Residue:		Filtrate:	
(PbSO ₄), HgS, S. Examine as in first scheme given for Group II.		Sn(C ₂ O ₄) ₂ . Evaporate + H ₂ SO ₄ until fumes of SO ₃ appear. Allow to become cold. Dilute + H ₂ O. Pass H ₂ S. Precipitate SnS ₂ . Yellow.	
Precipitate PbSO ₄ :		Residue:	
+ dilute H ₂ SO ₄ .		As ₂ S ₃ , Sb ₂ S ₃ . Dissolve in HCl + KClO ₃ . Boil to expel excess Cl. Introduce solution into H ₂ gas generating flask. Pass gases evolved through solution AgNO ₃ .	
Precipitate PbSO ₄ :		Filtrate:	
Bi(NO ₃) ₃ , Cu(NO ₃) ₂ , Cd(NO ₃) ₂ . Boil out excess HNO ₃ , dilute, neutralize + NaOH, and add excess KCN.		Precipitate: Ag ₃ Sb + HCl. Filter. Residue, AgCl. Reject. Solution: SbCl ₃ Confirm by 64 or 67.	
Precipitate PbSO ₄ :		Solution:	
Bi(OH) ₃ . Confirm Bi by 26.		Cu(CN) ₂ , 2KCN. Cd(CN) ₂ , 2KCN. Pass H ₂ S.	
Precipitate PbSO ₄ :		Solution:	
Cds. Yellow.		Cu(CN) ₂ , 2KCN. + NaClO × S. = Blue Solution. Boil = CuO and CuS. Black.	

Notes on Analysis of Group II.

I. At the time of the precipitation of the second group by H_2S , HNO_3 and other oxidizing agents should be absent, or present only in very small amounts. On boiling the solution down to a small bulk with HCl , these oxidizing agents are eliminated; HNO_3 , chlorine or chlorine oxides being volatilized, whereas chromates and permanganates are reduced.

The presence of oxidizing agents is objectionable because they oxidize the H_2S , forming H_2O , S , or even H_2SO_4 ; they also have a solvent effect on the sulphides formed, and so prevent a complete precipitation.

The best conditions for the precipitation of Group II. by H_2S are:—

Dilute solution.

Slightly acid + HCl .

Moderately warm.

II. Sulphides of the members of the second group are somewhat soluble in mineral acids unless the acids are quite dilute. CdS , Sb_2S_3 , and SnS_2 dissolve quite easily in HCl . HgS is insoluble in HNO_3 (concentrated HNO_3 may convert HgS on boiling to white basic compounds). PbS dissolves easily in HNO_3 —a portion of it, however, being converted into white insoluble PbSO_4 . Boiling saturated solution of oxalic acid dissolves SnS_2 , but does not affect As_2S_3 or Sb_2S_3 . $(\text{NH}_4)_2\text{S}_x$ dissolves easily SnS , SnS_2 , As_2S_3 , Sb_2S_3 , and small amounts of CuS . $(\text{NH}_4)_2\text{S}$, colorless, dissolves these last named, with the exception of SnS . Na_2S or K_2S dissolves SnS_2 , Sb_2S_3 , As_2S_3 , and appreciable amounts of HgS . CuS , CdS , Bi_2S_3 are insoluble in fixed alkaline sulphides.

Moist copper sulphide is easily oxidized by the oxygen of the air, forming CuSO_4 ; hence the sulphides of the second group should not be allowed to stand.

All sulphides are dissolved by oxidizing agents. (Exception: HNO_3 converts Sb_2S_3 and SnS_2 into the corresponding oxides, and does not dissolve HgS .)

III. NH_4OH dissolves hydroxides of Cu and Cd. KOH or NaOH dissolves hydroxides of Pb, Sn, and Sb. Neither NH_4OH nor KOH nor NaOH dissolves compounds of Hg and Bi.

(Arsenic compounds are not precipitated by alkaline hydroxides.)

IV. KCN precipitates solutions of Pb, Bi, Cu, and Cd. Bismuth precipitates as hydroxide with the evolution of HCN. The cyanides of Cu and Cd dissolve in excess, forming $\text{Cu}(\text{CN})_2 \cdot 2 \text{KCN}$, $\text{Cd}(\text{CN})_2 \cdot 2 \text{KCN}$.

V. Cupric salts, when treated with NH_4CNS and saturated with SO_2 , give a precipitate of $\text{Cu}_2(\text{CNS})_2$. White. This distinguishes Cu from all metals but those of the first group.

VI. Compounds of metals of the second group are easily reduced to the metallic state when heated on charcoal with Na_2CO_3 . Tin compounds require the addition of KCN. Bismuth easily oxidizes, yielding a yellow coat on the coal. Cadmium forms a coat on the coal which has a characteristic iridescence. Tin forms a white oxide that deposits near the reduced metal. This oxide, on being moistened with $\text{Co}(\text{NO}_3)_2$, gives a blue-green mass. Antimony easily oxidizes, forming a volatile white coat that collects on the coal for some distance from the reduced metal. This oxide, on being moistened with $\text{Co}(\text{NO}_3)_2$ and heated with the blow-pipe, gives an olive green mass. Arsenic compounds, on being reduced on the coal, give off a characteristic garlic-like odor. Copper compounds give no coat on the coal. For behavior of mercury compounds, see Note III. on Group I., and No. 17.

GROUP III.

IRON (Ferrous). Fe. Valence = II.

Use preferably FeSO_4 .

71. $(\text{NH}_4)_2\text{S}$ and fixed alkaline sulphides precipitate FeS .

Black.

Insoluble in excess of reagent.

Soluble in dilute mineral acids.

Oxidized by the air to FeSO_4 and basic ferric compounds.

72. Alkaline hydroxides precipitate $\text{Fe}(\text{OH})_2$. White, immediately changing to dirty green and finally to reddish brown. Due to oxidation.

Insoluble in excess of NaOH or KOH .

Soluble in NH_4OH in the presence of ammonium salts, the solution precipitating on exposure to air, due to formation of ferric compounds.

73. $\text{K}_3\text{Fe}(\text{CN})_6$ precipitates $\text{Fe}_3\text{Fe}_2(\text{CN})_{12}$.
Blue. (Distinction from ferric.)

74. All compounds of iron fused in a bead of borax, give in the reducing flame a pale green bead, and in the oxidizing flame one which is brown or yellow when hot, often colorless when cold.

75. Oxidizing agents, such as HNO_3 , Cl , Br , KClO_3 , $\text{K}_2\text{Mn}_2\text{O}_8$, $\text{K}_2\text{Cr}_2\text{O}_7$, convert ferrous into ferric compounds.

FERRIC. Fe . Valence = III.

Use preferably Fe_2Cl_6 .

76. $(\text{NH}_4)_2\text{S}$ and fixed alkaline sulphides precipitate $\text{FeS} + \text{S}$. See 71.

77. Alkaline hydroxides precipitate $\text{Fe}_2(\text{OH})_6$.
Reddish-brown.

Insoluble in excess of reagent.

Precipitation prevented by presence of organic substances, such as tartaric acid, citric acid, and sugar.

78. BaCO_3 suspended in water precipitates $\text{Fe}_2(\text{OH})_6$, with the evolution of CO_2 gas. (Distinction from ferrous compounds.)

All soluble carbonates precipitate $\text{Fe}_2(\text{OH})_6$ with evolutions of CO_2 .

79. KCNS or NH_4CNS produces $\text{Fe}_2(\text{CNS})_6$.
 Blood-red solution.
 Not destroyed by HCl .
80. $\text{NaC}_2\text{H}_3\text{O}_2$ in neutral solutions or those slightly acid with $\text{HC}_2\text{H}_3\text{O}_2$ produces $\text{Fe}_2(\text{C}_2\text{H}_3\text{O}_2)_6$, which is deep red. On being boiled, reddish brown basic ferric acetates are precipitated.
81. See 74.
82. Reducing agents, such as H_2S , SO_2 and nascent hydrogen, convert ferric into ferrous compounds.

ALUMINIUM. Al . Valence = III.

Use preferably $\text{Al}_2(\text{SO}_4)_3$.

83. $(\text{NH}_4)_2\text{S}$ and fixed alkaline sulphides precipitate $\text{Al}_2(\text{OH})_6$ with the evolution of H_2S gas.
 White, flocculent.
 Insoluble in excess of reagent.
84. Alkaline hydroxides precipitate $\text{Al}_2(\text{OH})_6$.
 White, flocculent.
 Slightly soluble in excess of NH_4OH (rendered less soluble by the presence of ammonium salts).
 Easily soluble in excess of NaOH and KOH ; hot or cold.
85. BaCO_3 suspended in water precipitates $\text{Al}_2(\text{OH})_6$ with the evolution of CO_2 .
86. Heated with blowpipe on charcoal, aluminium compounds yield, when moistened with $\text{Co}(\text{NO}_3)_2$ and again ignited, a sky-blue infusible mass.
87. $\text{Na}(\text{C}_2\text{H}_3\text{O}_2)$ analogous to ferric iron. See 80.

CHROMIUM. Cr.

Valence = III.

Use preferably $\text{Cr}_2(\text{SO}_4)_3$.

88. $(\text{NH}_4)_2\text{S}$ or fixed alkaline sulphides precipitate $\text{Cr}_2(\text{OH})_6$.
Grayish green.

Insoluble in excess of reagents.

Insoluble in hot NaOH or KOH .Soluble in excess of cold alkaline hydroxides. Re-precipitated by prolonged boiling. Slightly soluble in large excess of NH_4OH .

89. Alkaline hydroxides precipitate $\text{Cr}_2(\text{OH})_6$. See 88.
90. BaCO_3 suspended in water precipitates $\text{Cr}_2(\text{OH})_6$, with the evolution of CO_2 .
91. $\text{NaC}_2\text{H}_3\text{O}_2$ analogous to ferric iron. See 80.
92. Chromium compounds, heated on a loop of Pt wire with borax or microcosmic salt, dissolve, giving a clear emerald green bead.
93. Oxidizing agents, such as Cl , Br , NaClO , convert solutions of chromium salts to yellow alkaline chromates. Solid chromium compounds, fused with Na_2CO_3 and KNO_3 or KClO_3 , yield alkaline chromates, yellow, soluble in water.

NICKEL. Ni.

Valence = II.

Use preferably $\text{Ni}(\text{NO}_3)_2$.

94. $(\text{NH}_4)_2\text{S}$ or fixed alkaline sulphides precipitate NiS .
Black.

Insoluble in cold dilute HCl (1—6).

Insoluble in acetic acid.

Slightly soluble in excess of $(\text{NH}_4)_2\text{S}_x$, particularly in the presence of NH_4OH , giving inky brown solution.Distinction from Co . (The presence of ammonium salts hinders this solubility.)

Easily soluble in aqua regia.

95. NH_4OH precipitates $\text{Ni}(\text{OH})_2$, immediately soluble in excess, particularly in presence of ammonium salts, giving a blue solution.
96. NaOH or KOH precipitates $\text{Ni}(\text{OH})_2$.
Light green.
Insoluble in excess of reagent.
Soluble in ammonium salts.
97. KCN precipitates $\text{Ni}(\text{CN})_2$.
Yellowish green.
Insoluble in dilute HCl .
Soluble in excess of reagent.
This solution + excess NaOH or KOH , and treated with oxidizing agents such as Cl or Br or HgO , gives a precipitate of $\text{Ni}_2(\text{OH})_6$, black. (Distinction from Co .)
98. All nickel compounds dissolve completely in borax and microcosmic salt beads, imparting to them in the oxidizing flame a brownish color; in the reducing, a gray. (This color is obscured by the presence of Co compounds.)

COBALT. Co .

Valence = II.

Use preferably $\text{Co}(\text{NO}_3)_2$.

99. $(\text{NH}_4)_2\text{S}$ or fixed alkaline sulphides precipitate CoS .
Insoluble in cold dilute HCl (1—6).
Insoluble in acetic acid.
Insoluble in excess of reagent.
Easily soluble in aqua regia.
100. NH_4OH precipitates $\text{Co}(\text{OH})_2$ immediately soluble in excess, giving a reddish-brown solution.
101. NaOH or KOH precipitates blue basic salts.
Converted by boiling into $\text{Co}(\text{OH})_2$.
Pink.
Insoluble in excess of reagents.

102. KCN precipitates $\text{Co}(\text{CN})_2$.
Brownish-white.
Insoluble in dilute HCl.
Soluble in excess of reagent. This solution on prolonged boiling with a few drops of HCl is oxidized by the oxygen of the air to the soluble $\text{K}_3\text{Co}(\text{CN})_6$.
(Distinction from Ni.)
103. KNO_2 in solutions, acid only with acetic acid, precipitates $\text{K}_3\text{Co}(\text{NO}_2)_6$.
Yellow, crystalline.
Insoluble in acetic acid.
Soluble in HCl.
104. Cobalt compounds dissolve completely in borax and microcosmic salt beads, giving an intensely deep blue color, appearing black when large amounts of cobalt are present.

MANGANESE. Mn. Valence = II.

Use preferably MnSO_4 .

105. $(\text{NH}_4)_2\text{S}$ or fixed alkaline sulphides precipitate MnS .
Flesh-tint.
Insoluble in excess of reagents.
Easily soluble in dilute mineral acids and in acetic acid
(this latter a distinction from ZnS).
106. NH_4OH precipitates $\text{Mn}(\text{OH})_2$.
White.
Insoluble in excess of reagent.
Soluble in ammonium salts, hence precipitation does not take place in their presence. But on standing this solution becomes turbid and $\text{Mn}_2\text{O}_3(\text{OH})_2$, brown, separates because of atmospheric oxidation.
107. NaOH or KOH precipitates $\text{Mn}(\text{OH})_2$.
White, turning brown on exposure to air.
Insoluble in excess of reagents.

108. Manganese compounds, fused in a bead of microcosmic salt or borax, impart in the oxidizing flame an amethyst red color, which becomes colorless in the reducing flame.

If the hot microcosmic salt bead is laid on a crystal of KNO_3 or NaNO_3 , an intense violet coloration is developed.

109. Oxidizing agents, such as $\text{HNO}_3 + \text{PbO}_2$ or Pb_3O_4 , Cl or Br in alkaline solutions, convert solutions of manganous salts into permanganic acid or soluble permanganates, purple.

Solid compounds fused on Pt with $\text{Na}_2\text{CO}_3 + \text{KNO}_3$ or KClO_3 , form manganates, deep blue-green. Boiled with water these dissolve, forming purple permanganates and insoluble MnO_2 .

Bromine precipitates from acetic acid solutions, MnO_2 , brown.

ZINC. Zn .

Valence = II.

Use preferably ZnSO_4 .

110. $(\text{NH}_4)_2\text{S}$ or fixed alkaline sulphides precipitate ZnS .
White.

Insoluble in excess of reagents.

Insoluble in acetic acid.

(Distinction from MnS .)

Easily soluble in dilute min. acids.

111. NH_4OH or fixed alkaline hydroxides precipitate $\text{Zn}(\text{OH})_2$.

White.

Readily soluble in excess of reagents.

112. Heated on charcoal with Na_2CO_3 , ZnO is produced, yellow while hot, white when cold; moistened with $\text{Co}(\text{NO}_3)_2$ and heated again, it gives a green infusible mass.

Analysis of Group III.

+ NH_4OH in slight excess.
 + $(\text{NH}_4)_2\text{S}$ in slight excess. Warm, and allow precipitate to settle.
 Precipitate = FeS , $\text{Al}_2(\text{OH})_6$, $\text{Cr}_2(\text{OH})_6$, CoS , NiS , ZnS , MnS .
 (Filtrate to be examined for following groups.)
 Precipitate + cold dilute HCl (1-6).

<p>Residue:</p> <p>NiS, CoS. Dissolve in aqua regia. Boil to dryness. Dissolve in water. + excess KCN, then NaClO. Digest with HgO.</p>	<p>Filtrate:</p> <p>FeCl_3, Al_2Cl_6, Cr_2Cl_6, ZnCl_2, MnCl_2. Boil out H_2S. + excess KOH or NaOH and NaClO or KClO. Boil.</p>		
<p>Precipitate:</p> <p>$\text{Ni}_2(\text{OH})_6$. Black. Confirm by 98.</p>	<p>Residue:</p> <p>$\text{Fe}_2(\text{OH})_6$, $\text{Mn}_2\text{O}_4(\text{OH})_2$. Dissolve + HCl and boil out Cl. Allow to cool. Neutralize with Na_2CO_3. Add $\text{NaC}_2\text{H}_3\text{O}_2$. Boil.</p>	<p>Filtrate:</p> <p>$\text{Al}_2(\text{ONa})_6$, Na_2CrO_4, $\text{Zn}(\text{ONa})_2$. + NH_4Cl in excess, and warm.</p>	
	<p>Precipitate:</p> <p>Basic Ferric acetate. Brown. Flocculent. Dissolve in HCl, and confirm by 79.</p>	<p>Precipitate:</p> <p>$\text{Al}_2(\text{OH})_6$. White. Gelatinous. Confirm by 86.</p>	<p>Filtrate:</p> <p>+ $\text{HC}_2\text{H}_3\text{O}_2$ in excess. + H_2S gas to saturation.</p>
	<p>Filtrate:</p> <p>+ NaOH till alkaline, then $(\text{NH}_4)_2\text{S}$. MnS. Flesh tint. Confirm by 108.</p>	<p>Precipitate:</p> <p>ZnS, white. Confirm by 112.</p>	<p>Filtrate:</p> <p>$\text{Cr}_2(\text{C}_2\text{H}_3\text{O}_2)_6$ + NH_4OH $\text{Cr}_2(\text{OH})_6$. Green. Flocculent. Confirm by 92.</p>

Alternative Analysis of Group III.

+ NH_4OH in slight excess.

+ $(\text{NH}_4)_2\text{S}$ in slight excess. Warm, and allow precipitate to settle.

Precipitate = FeS , $\text{Al}_2(\text{OH})_6$, $\text{Cr}_2(\text{OH})_6$, CoS , NiS , ZnS , MnS .

(Filtrate to be examined for following groups.)

+ Aqua regia and boil out chlorine and excess of acid.

Fe_2Cl_6 , Al_2Cl_6 , Cr_2Cl_6 , CoCl_2 , NiCl_2 , ZnCl_2 , MnCl_2 .

+ BaCO_3 suspended in water. Shake well in flask. Allow to stand.

Precipitate:	
$\text{Fe}_2(\text{OH})_6$, $\text{Cr}_2(\text{OH})_6$, $\text{Al}_2(\text{OH})_6$. Excess BaCO_3 . Boil + excess KOH .	
Residue:	
$\text{Fe}_2(\text{OH})_6$, $\text{Cr}_2(\text{OH})_6$. Fuse + KNO_3 and Na_2CO_3 . Extract + H_2O .	Filtrate: $\text{Al}_2(\text{ONa})_6$, $+\text{NH}_4\text{Cl}$. Boil =. $\text{Al}_2(\text{OH})_6$. Confirm by 86.
	Filtrate: K_2CrO_4 , Na_2CrO_4 . Confirm Cr by 11.
Filtrate:	
NiCl_2 , CoCl_2 , ZnCl_2 , MnCl_2 , BaCl_2 . Add a large quantity of acetic acid. + H_2S through cold mod. dilute solution.	
Precipitate:	
ZnS . See 110 and 112.	Filtrate: $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2$, $\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2$, $\text{Mn}(\text{C}_2\text{H}_3\text{O}_2)_2$. Nearly neutralize with Na_2CO_3 . Warm solution. Pass H_2S .
	Precipitate: NiS , CoS . Dissolve in aqua regia. Boil out Cl. Make alkaline + KOH . Filter. Dissolve precipitate in $\text{HC}_2\text{H}_3\text{O}_2$ + KNO_3 . Allow to stand.
Filtrate:	
Precipitate: $\text{K}_2\text{Co}(\text{NO}_2)_6$. Confirm by bead. See 104.	Filtrate: $+\text{KOH} = \text{Ni}(\text{OH})_2$. Confirm by bead. See 98.



Scheme for Analysis of Third Group in Presence of (a) Oxalic Acid, (b) Phosphoric Acid.

+ NH_4OH until alkaline (NH_4)₂S in slight excess. Warm and allow to settle. Filter and wash with water containing a little (NH_4)₂S.

Precipitate: Treat + cold, dilute HCl (1—6).		Filtrate: Reserve for examination of Groups IV. and V.
Residue: NiS, CoS. Examine according to methods previously given.	Filtrate: Examine small portion, after boiling out H_2S , for (a) oxalic acid by adding a slight excess of NH_4OH and then acidifying with acetic acid + CaCl_2 , a white precipitate = CaC_2O_4 .	

If oxalic acid is found to be present, evaporate entire filtrate to dryness and ignite gently to decompose oxalates. Allow dish to become cold; dissolve in dilute HCl and proceed, using either of the previous schemes of analysis.

(b) Examine a small portion of filtrate according to 191. If phosphoric acid is found to be present, use the following scheme of analysis.

(Note.—If oxalic acid and phosphoric acid are both present, destroy the oxalic acid according to method given above and then analyze the solution according to the method following.)

Boil the filtrate with a few drops of HNO_3 , and examine a small portion for Fe according to 79.

Add to remainder of filtrate Fe_2Cl_6 , neutralize with Na_2CO_3 , acidify slightly with acetic acid, add $\text{NaC}_2\text{H}_3\text{O}_2$ and boil.

Precipitate: Examine for Al, Cr. Heat with excess of NaOH + NaClO. Filter and reject the precipitate. To filtrate, add NH_4Cl , in excess, boil and filter.		Filtrate: Examine for Mn, Zn, Ba, Sr, Ca, Mg, according to methods used in the regular systematic grouping.
Precipitate: White, flocculent, shows presence of Al.	Filtrate: Na_2CrO_4 . Acidify with $\text{HC}_2\text{H}_3\text{O}_2$ and examine for Cr, according to 11.	

Alternative Method for Use in Presence of Oxalates and Phosphates.

Treat the filtrate from Group II. with Sn and HNO_3 . Evaporate to dryness and gently ignite. The oxalic acid will be decomposed and the phosphoric acid removed as phosphate of tin. Take up with dilute HNO_3 and examine the filtrate according to the regular systematic grouping.

Notes on Analysis of Group III.

I.—For action of $(\text{NH}_4)_2\text{S}$ on the members of this group, compare Nos. 71, 76, 83, 88, 94, 99, 105, 110.

Tartaric acid, citric acid, and other organic matter, such as sugar, prevent the precipitation of hydroxides but not of sulphides, therefore Al and Cr are not precipitated by the group reagent in the presence of these matters.

If any of the above are found to be present, evaporate to dryness and destroy by ignition. Take up with dilute HCl and proceed with the regular scheme.

II.—If phosphates or oxalates be present, the fourth group will be precipitated on the addition of NH_4OH , and thus will be found with the third group. (See Nos. 116, 117, 121, 122, 126, 127.) Magnesium compounds are also similarly precipitated in the presence of phosphates. (See 131.)

In this case analyze the precipitate formed by the addition of third group reagents, according to the schemes given for use when phosphates or oxalates are present.

III.— BaCO_3 suspended in water precipitates, as hydroxides, salts derived from oxides of the type R_2O_3 , (Fe, Al, Cr); but not salts derived from oxides of the type RO .

IV.—When compounds of this group are fused with a mixture of alkaline carbonate and nitrate, two of them give rise to combinations which dissolve in water, viz., Mn and Cr, which form respectively Na_2MnO_4 and Na_2CrO_4 . The former

dissolves in water, giving a purple solution of $\text{Na}_2\text{Mn}_2\text{O}_8$, with the simultaneous precipitation of MnO_2 . The Na_2CrO_4 dissolves in water giving a yellow solution. The other members of this group are converted by this treatment into oxides, insoluble in water.

V.—All of the members of this group give colored characteristic beads with the exception of Al and Zn. See Nos. 74, 92, 98, 104, 108.

GROUP IV.

BARIUM. Ba. Valence = II.

Use preferably BaCl_2 .

113. $(\text{NH}_4)_2\text{CO}_3$ or fixed alkaline carbonates precipitate BaCO_3 .

White, pulverulent.

Insoluble in excess of reagents.

Insoluble in alkaline hydroxides.

Soluble in acids.

Soluble in solutions containing CO_2 , with the formation of $\text{Ba}(\text{HCO}_3)_2$. This is decomposed by boiling or by the addition of soluble hydroxides with the re-precipitation of BaCO_3 .

Slightly soluble in NH_4Cl .

114. H_2SO_4 precipitates BaSO_4 .

White, pulverulent.

Insoluble in acids (with the exception of concentrated H_2SO_4).

115. K_2CrO_4 precipitates BaCrO_4 , distinction from Sr and Ca.

116. $(\text{NH}_4)_2\text{C}_2\text{O}_4$ precipitates BaC_2O_4 .

White, pulverulent.

Soluble in HCl ; solution hastened by warming.

Insoluble in NH_4OH .

117. Na_2HPO_4 precipitates BaHPO_4 .
 White, flocculent.
 Soluble in acids.
 Insoluble in NH_4OH .
118. Ba compounds moistened with HCl on the loop of a clean platinum wire, impart to the flame a yellowish-green color.

STRONTIUM. Sr. Valence = II.

Use preferably SrCl_2 .

119. $(\text{NH}_4)_2\text{CO}_3$ or fixed alkaline carbonates.
 (Analogous to Ba. See 113.)
120. H_2SO_4 precipitates SrSO_4 .
 White, pulverulent.
 Very slightly soluble in water.
 Strontium compounds are *immediately* precipitated by a solution of CaSO_4 .
121. $(\text{NH}_4)_2\text{C}_2\text{O}_4$ precipitates SrC_2O_4 .
 (Analogous to Ba. See 116.)
122. Na_2HPO_4 precipitates SrHPO_4 .
 (Analogous to Ba. See 117.)
123. $\text{Sr}(\text{NO}_3)_2$ is insoluble in alcohol.
 (Distinction from calcium.)
124. Strontium compounds moistened with HCl , and heated on a Pt wire, impart a crimson color to the flame.

CALCIUM. Ca. Valence = II.

Use preferably CaCl_2 .

125. $(\text{NH}_4)_2\text{CO}_3$ or fixed alkaline carbonates precipitate CaCO_3 .
 (Analogous to Ba and Sr. See 113.)
126. $(\text{NH}_4)_2\text{C}_2\text{O}_4$ precipitates CaC_2O_4 .
 (Analogous to Ba and Sr. See 116.)
 Insoluble in acetic acid.



127. Na_2HPO_4 precipitates CaHPO_4 .
(Analogous to Ba and Sr. See 117.)
128. $\text{Ca}(\text{NO}_3)_2$ is soluble in alcohol. (Distinction from strontium.)
129. H_2SO_4 precipitates CaSO_4 only from concentrated solutions on addition of rather strong H_2SO_4 .
Decidedly soluble in water.
130. Calcium compounds moistened with HCl , and heated on a Pt wire, impart a brick-red color to the Bunsen flame.

Analysis of Fourth Group.

+ HCl to slightly acid reaction.

Boil to separate sulphur.

Filter. Render alkaline with NH_4OH .

Filtrate BaCl_2 , SrCl_2 , CaCl_2 and Group V.

+ $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and warm gently.

Precipitate BaC_2O_4 , SrC_2O_4 , CaC_2O_4 .

Ignite in a porcelain dish.

Dissolve in $\text{HC}_2\text{H}_3\text{O}_2$.

Filtrate.

Examine for
Group V.

+ K_2CrO_4

Precipitate:

BaCrO_4 .

See 115.

Filtrate

SrCrO_4 , CaCrO_4 .

+ NH_4OH to alkaline reaction.

+ $(\text{NH}_4)_2\text{C}_2\text{O}_4$.

Precipitate SrC_2O_4 , CaC_2O_4 .

Dissolve in dilute HNO_3 .

Evaporate to dryness on steam-bath.

Digest + $\text{C}_2\text{H}_5\text{OH}$ absolute.

Residue:

$\text{Sr}(\text{NO}_3)_2$.

Confirm by 120 or
124.

Filtrate:

$\text{Ca}(\text{NO}_3)_2$, H_2O . ater.

Confirm by 126 or
130.

Notes.

I.—In the scheme of analysis given for the fourth group, $(\text{NH}_4)_2\text{C}_2\text{O}_4$ is used in preference to $(\text{NH}_4)_2\text{CO}_3$, chiefly on account of the greater insolubility of the oxalates.

II.—The fact of the different solubilities of the chlorides and nitrates of the members of this group in absolute alcohol is conveniently taken advantage of in methods of analysis of this group. Thus:—

BaCl_2 , insoluble in alcohol.

SrCl_2 } soluble in alcohol.
 CaCl_2 }

$\text{Sr}(\text{NO}_3)_2$, insoluble in alcohol.

$\text{Ca}(\text{NO}_3)_2$, soluble in alcohol.

III.—The colors imparted to the Bunsen flame are characteristic and are specially important as confirmatory tests. (See Nos. 118, 124, 130.)

GROUP V.

MAGNESIUM. Mg. Valence = II.

Use preferably MgSO_4 .

131. Na_2HPO_4 in the presence NH_4OH and NH_4Cl precipitates MgNH_4PO_4 . White, crystalline. Converted by heat into $\text{Mg}_2\text{P}_2\text{O}_7$.
132. Alkaline carbonates, oxalates or hydroxides fail to precipitate Mg solutions in the presence of salts of ammonium.
133. Solutions of Mg compounds containing an excess of $(\text{NH}_4)_2\text{C}_2\text{O}_4$, leave on evaporation to dryness and ignition of the residue, white MgO , practically insoluble in water.
134. Compounds of magnesium ignited with $\text{Co}(\text{NO}_3)_2$ on charcoal yield a rose pink infusible mass.

POTASSIUM. K.

Valence = I.

Use preferably KCl.

135. PtCl_4 precipitates K_2PtCl_6 . Yellow, heavy.
 Insoluble in alcohol. (Distinction from Na.) Slightly soluble in cold water. Readily soluble in hot water, from which solution it crystallizes in yellow octahedra. (Similar compound with similar properties formed with NH_4Cl .)
136. Potassium compounds moistened with HCl give, when heated in the Bunsen flame on a Pt wire, a lilac coloration.

SODIUM. Na.

Valence = I.

Use preferably NaCl.

137. PtCl_4 forms Na_2PtCl_6 , which, on evaporation, crystallizes in needle-shaped prisms.
 Aurora-red.
 Readily soluble in water and in alcohol.
 (Distinction from K. See 135.)
138. Sodium compounds moistened with HCl, and heated on a Pt wire in the Bunsen flame, impart a strong daffodil yellow color.

AMMONIUM. NH_4 .

Valence = I.

Use preferably NH_4Cl .

139. PtCl_4 forms $(\text{NH}_4)_2\text{PtCl}_6$ similar to K compound.
140. All NH_4 salts on being boiled + excess KOH or NaOH, yield NH_3 gas, recognized by its characteristic odor, turning red litmus blue, or paper moistened with CuSO_4 deep blue, or with mercurous nitrate black. With HCl, white fumes of NH_4Cl are formed.

Analysis of Group V.

+ $(\text{NH}_4)_2\text{C}_2\text{O}_4$ in excess.

Evaporate to dryness. Ignite to expel ammonium salts.

Extract with water.

Residue: MgO. Confirm by 134, or dissolve in HCl.	Filtrate Na_2CO_3 , K_2CO_3 . + HCl to acid reaction. Evaporate to dryness on water-bath + PtCl_4 .	
Add NH_4OH and confirm by 131.	Add $\text{C}_2\text{H}_5\text{OH}$ to residue. Precipitate K_2PtCl_6 . See No. 135.	Filtrate Na_2PtCl_6 . Evaporate sponta- neously. See 137.

Note.—Examine for ammonium compounds in the original solution. (See 140.)

Notes.

I.—Dry oxalates decompose on ignition with the evolution of CO and the production of carbonates. In most cases these carbonates are decomposed with the evolution of CO_2 and production of oxides. (See analyses given for Group V. Also compare analysis of Groups III., IV., V., in presence of oxalates.)

II.— NH_4Cl must be removed by ignition before testing for K and Na, as it forms a similar compound with PtCl_4 .

III.—All ammonium salts are volatile on ignition.

IV.—Nessler's solution ($\text{HgI}_2 \cdot 2 \text{KI} + \text{excess KOH}$) produces a brown precipitate of NHg_2I with ammonium compounds.

An extremely delicate test. Traces of NH_3 give a yellow or brown coloration.

V.—The colors imparted to the Bunsen flame are characteristic and are of special importance as confirmatory tests. (See 136 and 138.)

B.—Reactions of the Acids.

ACETIC ACID. $\text{HC}_2\text{H}_3\text{O}_2$.

Use preferably $\text{NaC}_2\text{H}_3\text{O}_2$.

141. $\text{H}_2\text{SO}_4 + \text{C}_2\text{H}_5\text{OH}$ form, on gently warming, ethyl acetate, $\text{C}_2\text{H}_5\text{C}_2\text{H}_3\text{O}_2$, possessing a characteristic, fragrant odor.
142. Fe_2Cl_6 forms $\text{Fe}_2(\text{C}_2\text{H}_3\text{O}_2)_6$, a deep red solution, which on boiling is converted into basic ferric acetate.
(See 80.)
143. AgNO_3 , in rather concentrated solutions, precipitates $\text{AgC}_2\text{H}_3\text{O}_2$.
White, crystalline.
Easily soluble in HNO_3 .
144. Acetates yield on ignition either carbonates or oxides, without blackening.

ARSENIC ACID. H_3AsO_4 .

Use preferably Na_3AsO_4 .

145. H_2S in acid solutions first effects a reduction with separation of sulphur, and subsequently precipitates As_2S_3 .
(See 45.)
146. MgSO_4 in presence of NH_4OH and NH_4Cl precipitates $\text{MgNH}_4\text{AsO}_4$.
(See 47.)
(Distinction from *arsenious* acid.)
This precipitate ignited forms $\text{Mg}_2\text{As}_2\text{O}_7$. Heated on charcoal it is decomposed with the production of a characteristic garlic-like odor.
147. AgNO_3 precipitates Ag_3AsO_4 .
Reddish brown.
Easily soluble in HNO_3 .

Easily soluble in NH_4OH .

Slightly soluble in NH_4NO_3 .

148. Arsenic acid is converted into arsenious acid by reducing agents, such as H_2S , SO_2 , FeSO_4 .
For other reactions, see As, page 13.

ARSENIOUS ACID. H_3AsO_3 .

Use preferably Na_3AsO_3 .

149. H_2S in acid solutions immediately precipitates As_2S_3 .
(Distinction from arsenic acid. See 39.)
150. AgNO_3 precipitates Ag_3AsO_3 .
Yellow.
Easily soluble in HNO_3 .
Easily soluble in NH_4OH .
Slightly soluble in NH_4NO_3 .
151. Oxidizing agents, such as Fe_2Cl_6 , $\text{K}_2\text{Mn}_2\text{O}_8$, or $\text{K}_2\text{Cr}_2\text{O}_7$ in acid solutions, also Cl, Br, I and NaClO in acid or alkaline solutions, convert arsenious acid into arsenic acid.
For other reactions, see As, pages 12 and 13.

BORIC ACID. H_3BO_3 .

Use preferably $\text{Na}_2\text{B}_4\text{O}_7$.

152. AgNO_3 in moderately concentrated solutions precipitates AgBO_2 .
White.
Soluble in HNO_3 .
153. BaCl_2 in moderately concentrated solutions precipitates $\text{Ba}(\text{BO}_2)_2$.
White.
Soluble in HCl or HNO_3 .
154. Turmeric paper moistened with solutions slightly acid with HCl , develops, on drying at a gentle heat, a fine rose-red color.

155. Solid borates moistened with concentrated H_2SO_4 and mixed with a little glycerine or alcohol and set on fire, give a flame which is greenish on the edges.
156. A bead of a mixture of KHSO_4 and CaF_2 (4—1) dipped into a solid borate and then heated in a Bunsen flame, gives a greenish color which is instantly developed on the edges.

CARBONIC ACID. H_2CO_3 .

Use preferably Na_2CO_3 .

157. AgNO_3 precipitates Ag_2CO_3 .
White.
Soluble in HNO_3 .
Soluble in NH_4OH .
158. BaCl_2 precipitates BaCO_3 .
White, pulverulent.
(See 113.)
159. Carbonates give with dilute acids an evolution of CO_2 gas, which passed into $\text{Ca}(\text{OH})_2$ gives a precipitate of CaCO_3 .
(See 125.)

CHROMIC ACID. H_2CrO_4 .

Use preferably K_2CrO_4 .

160. AgNO_3 precipitates dark red Ag_2CrO_4 .
161. BaCl_2 precipitates BaCrO_4 . (See 115.)
162. $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ precipitates PbCrO_4 .
Yellow.
Insoluble in dilute acids.
Soluble in KOH or NaOH .
163. Reducing agents, such as H_2S , SO_2 , H_3AsO_3 , nascent hydrogen, in acid solutions, convert chromates (yellow or red) to chromium salts (green or violet).

HYDROBROMIC ACID. HBr .

Use preferably NaBr .

164. AgNO_3 precipitates AgBr .

Pale yellow.

Insoluble in HNO_3 .

Soluble with difficulty in NH_4OH .

165. Chlorine or chlorine oxides (acid solutions of hypochlorites or chlorates) liberate bromine which dissolves in CS_2 or CHCl_3 , coloring it a reddish brown.

166. Concentrated H_2SO_4 decomposes solid bromides, giving reddish brown vapors of bromine.

Passed into dilute NH_4OH forms NH_4Br .

Colorless. (See 168.)

HYDROCHLORIC ACID. HCl .

Use preferably NaCl .

167. AgNO_3 precipitates AgCl . (See 1.)

168. Solid chlorides mixed with solid $\text{K}_2\text{Cr}_2\text{O}_7$ and covered with concentrated H_2SO_4 , yield, on gently warming, CrO_2Cl_2 .

Blood-red gas.

Passed into dilute NH_4OH forms $(\text{NH}_4)_2\text{CrO}_4$.

Yellow solution. (See 162.)

169. Concentrated H_2SO_4 decomposes solid chlorides, giving off fumes of HCl gas.

HYDROCYANIC ACID. HCN .

Use preferably KCN .

170. AgNO_3 precipitates AgCN . (See 4.)

171. FeSO_4 and Fe_2Cl_6 added to a solution of a cyanide, alkaline with KOH or NaOH , and then acidified with HCl , form $\text{Fe}_4(\text{FeC}_6\text{N}_6)_3$, "Prussian Blue."

172. Alkaline cyanides mixed with $(\text{NH}_4)_2\text{S}$ and evaporated to dryness on the water-bath produce NH_4CNS . (See 79.)

173. H_2SO_4 decomposes solid cyanides, giving off HCN gas.
(Danger! *Highly poisonous!!*)

HYDROFLUORIC ACID. HF.

Use preferably CaF_2 .

174. Solid fluorides mixed with concentrated H_2SO_4 in a lead dish yield, on gently warming, HF, hydrofluoric acid gas, which etches glass.
175. (See 156.)

HYDRIODIC ACID. HI.

Use preferably NaI.

176. AgNO_3 precipitates AgI.
Straw yellow.
Insoluble in HNO_3 .
Very slightly soluble in NH_4OH .
177. Chlorine or chlorine oxides (see 165) liberate iodine which dissolves in CS_2 or CHCl_3 , coloring it violet or purple. The color is destroyed by excess of Cl, ICl_3 being formed. These decompositions take place before the similar reactions with bromides.
178. Starch made into a thin paste with water, boiled and then cooled, is colored an intense indigo blue by free iodine.
179. Concentrated H_2SO_4 decomposes solid iodides, giving violet vapors of iodine, which soon condense as a dark colored solid.

HYDROSULPHURIC ACID. H_2S .

Use preferably FeS.

180. Sulphides warmed with concentrated HCl give off H_2S gas.
Characteristic odor.
Papers moistened with $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ are blackened by the gas.

181. Solid sulphides fused + Na_2CO_3 in a porcelain dish yield Na_2S . Fused mass placed on Ag and moistened gives black stain of Ag_2S .

NITRIC ACID. HNO_3 .

Use preferably KNO_3 .

182. On adding a few drops of a solution of a nitrate to concentrated H_2SO_4 , containing a clear crystal of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, a brown ring around the crystal is developed, due to the formation of $\text{FeSO}_4(\text{NO})_2$ —an exceedingly unstable compound easily decomposed by heat, setting free NO, which on contact with the oxygen of the air forms brown fumes of NO_2 .

OXALIC ACID. $\text{H}_2\text{C}_2\text{O}_4$.

Use preferably $(\text{NH}_4)_2\text{C}_2\text{O}_4$.

183. BaCl_2 precipitates BaC_2O_4 .
White, pulverulent.
Easily soluble in HCl and HNO_3 .
184. AgNO_3 precipitates $\text{Ag}_2\text{C}_2\text{O}_4$.
White.
Easily soluble in HNO_3 .
Easily soluble in NH_4OH .
185. CaCl_2 precipitates CaC_2O_4 .
Insoluble in $\text{HC}_2\text{H}_3\text{O}_2$.
Insoluble in NH_4OH .
Soluble in HCl and HNO_3 .
186. Solid oxalates warmed with concentrated H_2SO_4 are broken up, yielding CO_2 and CO gases. If MnO_2 is mixed with the powder, CO_2 only is produced.
187. Oxalates and oxalic acid ignited decompose without separation of carbon.

PHOSPHORIC ACID. H_3PO_4 .

Use preferably Na_2HPO_4 .

188. BaCl_2 precipitates BaHPO_4 .

White, pulverulent.

Easily soluble in acids.

189. AgNO_3 precipitates Ag_3PO_4 .

Yellow.

Easily soluble in NH_4OH and in acids.

190. Mg salts in the presence of NH_4OH and NH_4Cl precipitate MgNH_4PO_4 .

White, crystalline.

Insoluble in NH_4OH .

Soluble in acids.

Ignited, forms $\text{Mg}_2\text{P}_2\text{O}_7$, which, moistened with $\text{Co}(\text{NO}_3)_2$ and heated on charcoal, gives a blue mass. (Distinction from As. See 146.)

191. $(\text{NH}_4)_2\text{MoO}_4$ in HNO_3 solution precipitates, on warming, $(\text{NH}_4)_3\text{PO}_4 \cdot 11\text{MoO}_3$.

Yellow, pulverulent.

Insoluble in HNO_3 .

Soluble in NH_4OH and in fixed alkalis.

H_3AsO_4 gives similar results.

SILICIC ACID. H_2SiO_3 .

Use preferably Na_2SiO_3 .

192. BaCl_2 precipitates BaSiO_3 .

White.

193. HCl decomposes moderately concentrated solutions, silicates forming H_2SiO_3 .

White, gelatinous. On evaporation to dryness, SiO_2 remains as a white insoluble powder. Heat on charcoal with $\text{Co}(\text{NO}_3)_2$, SiO_2 , or any silicate, gives a blue mass.

194. Silicates heated in a bead of microcosmic salt are decomposed with the separation of SiO_2 , which floats about in the hot bead, unaffected.

SULPHURIC ACID. H_2SO_4 .

Use preferably Na_2SO_4 .

195. BaCl_2 precipitates BaSO_4 .
(See 114.)
196. Sulphates fused with Na_2CO_3 on charcoal are reduced to sulphides.
(See 181.)
The fused mass placed on silver coin and moistened with water, produces a black stain of Ag_2S .

TARTARIC ACID. $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$.

Use preferably $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$.

197. BaCl_2 precipitates $\text{BaC}_2\text{H}_4\text{O}_6$.
White.
Soluble in HCl and HNO_3 .
198. AgNO_3 precipitates from neutral tartrates $\text{Ag}_2\text{C}_4\text{H}_4\text{O}_6$.
White.
Easily soluble in HNO_3 and in NH_4OH .
The ammoniacal solution of this precipitate on being gently warmed forms on the side of the containing vessel an adherent brilliant coating of metallic silver.
If boiled, metallic silver is precipitated in the form of a black powder.
199. KCl precipitates white, crystalline $\text{KHC}_4\text{H}_4\text{O}_6$.
200. $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$, or solid tartrates, yield on ignition a black residue and give off a characteristic odor of burnt sugar, accompanied by much intumescence.

Analysis of the Acids.

(a) ARSENIC ACID.

Boil a portion of the original solution with an excess of Na_2CO_3 . To the filtrate add NH_4OH , NH_4Cl , MgSO_4 . Test the precipitate formed for $\text{MgNH}_4\text{AsO}_4$. (See No. 146.) This precipitate may also contain MgNH_4PO_4 .

(b) ARSENIOS ACID.

Acidify the filtrate from the precipitate caused by the addition of MgSO_4 with HCl , warm and pass H_2S ; a yellow precipitate is As_2S_3 . Confirm by 149.

(c) CHROMIC ACID.

To the filtrate from the As_2S_3 in (b), add NH_4OH till alkaline. (See 163 and 89, 88, 92.)

(d) CARBONIC ACID.

Add dilute HCl to a portion of the original solution and pass the gas evolved through a solution of $\text{Ca}(\text{OH})_2$. (See 159.)

(e) HYDROFLUORIC ACID.

Evaporate a portion of the original solution to dryness and examine the powder obtained by 174.

(f) HYDROSULPHURIC ACID.

(See 180.)

(g) NITRIC ACID.

To a portion of the original solution, add a slight excess of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$. Filter and remove the excess of Pb from the filtrate with dilute H_2SO_4 . Concentrate the filtrate and examine according to 182.

(h) ACETIC ACID.

To a portion of the original solution, add a slight excess of $\text{Pb}(\text{NO}_3)_2$. Filter and examine the filtrate by 141 or 142.

Treat the remainder of the original solution in the following manner:—

Dilute the solution, warm and saturate with H_2S . Reject the precipitate, and to the filtrate add an excess of Na_2CO_3 . Boil and filter. Reject the precipitate as before, neutralize the filtrate with HNO_3 , and examine the solution for the remaining acids as indicated below.

(i) BORIC ACID.

Examine a portion of the solution according to 154, or evaporate a portion to dryness and examine according to 155 or 156.

(j) HYDRIODIC ACID.—(k) HYDROBROMIC ACID.

Examine a portion of the solution according to 177 and 165.

(l) HYDROCHLORIC ACID.

Examine a portion of the solution according to 167, or, preferably,

Evaporate a portion of the solution and examine according to 168.

(m) HYDROCYANIC ACID.

To a portion of the solution add concentrated H_2SO_4 , warm gently and pass the gas evolved into KOH . Examine this solution according to 171 or 172.

(n) OXALIC ACID.

Acidify a portion of the solution with acetic acid and add CaCl_2 . (See 185.)

This precipitate on ignition forms CaCO_3 , which effervesces with acid.

Evaporate a portion of the solution and examine according to 186.

(o) PHOSPHORIC ACID.

Examine a portion according to 190 or 191 (in absence of silicic acid).

(p) SILICIC ACID.

Evaporate a portion of the solution to dryness and examine according to 194.

(q) SULPHURIC ACID.

Examine a portion of the solution according to 195, or evaporate to dryness and examine according to 196.

(r) TARTARIC ACID.

Evaporate a portion of the solution to dryness and examine according to 200.

Notes on Analysis of the Acids.

I. Na_2CO_3 is used to precipitate the bases before the examination for certain acids. Arsenic and arsenious compounds are not removed by this treatment. In the presence of organic acids or ammonium salts, certain metals, such as Cu, Hg, Fe, etc., are not removed by this treatment; hence the first treatment with H_2S , by means of which the above are removed as sulphides.

II. Chromic acid compounds are reduced by H_2S to chromium salts. The change in color from yellow or red of the chromate to green or purple of the chromium salt is characteristic, and the resultant solution answers to any of the regular tests for chromium salts.

III. HCN produces a turbidity in lime water similar to that produced by CO_2 . (See Cl.) In case this acid is present, add *an excess* of AgNO_3 , whereby both the AgCN and Ag_2CO_3 are precipitated. Shake and allow precipitate to settle. Decant the clear liquid. On adding HNO_3 dilute to the precipitate, the carbonate dissolves with effervescence, setting free CO_2 . The cyanide is unaffected.

IV. Before testing for HNO_3 , the addition of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ effects the removal of chromates, bromides, and iodides.

The first of these would be reduced by the $\text{FeSO}_4 + \text{H}_2\text{SO}_4$ to a dark-colored solution, while the bromides and iodides would yield bromine and iodine, which would give misleading indications. Before examining for $\text{HC}_2\text{H}_3\text{O}_2$, $\text{Pb}(\text{NO}_3)_2$ is added to effect the removal of the same substances which also interfere with the examination for this acid. Chromic acid, bromine, and iodine, being oxidizing agents, prevent the formation of the ethyl acetate, and are therefore removed.

V. When a dry chloride mixed with dry $\text{K}_2\text{Cr}_2\text{O}_7$ is moistened with concentrated H_2SO_4 , CrO_2Cl_2 , a blood-red gas is given off. Bromides and iodides do not form analogous compounds. They are decomposed by concentrated H_2SO_4 , setting free bromine and iodine respectively. These colored vapors might easily be mistaken for the gas CrO_2Cl_2 , hence the subsequent treatment with ammonia, the formation of a chromate with its characteristic yellow color, and precipitations yielded by such metals as Pb. The bromine and iodine dissolve in the NH_4OH with the formation of colorless compounds.

VI. In examining for phosphoric acid with $(\text{NH}_4)_2\text{HMoO}_4$, silicic acid should be absent, as it forms a similar yellow precipitate. If silicic acid is present, it should be removed by 193.

VII. Tartaric acid is decomposed on ignition with blackening; acetic and oxalic acids decompose without blackening. Organic matter, such as dust accumulated from the air, or filter paper, decomposes with blackening, but without the characteristic odor of "burnt sugar."

VIII. All solid sulphides heated in air or oxygen yield SO_2 .

Solubility of the Metals in the Common Mineral Acids.

HCl, HNO₃, H₂SO₄.

1. HNO₃ is the general solvent for the metals. All the metals dissolve in this acid, with evolution of nitrogen oxides, with the exception of Sn and Sb, which form insoluble oxides, and Au and Pt, which are unaffected.

2. HCl is not so general a solvent for the metals.

Cd, As, Sn, Fe, Al, Cu, Mn, Zn and fourth and fifth group metals dissolve in HCl.

Ni and Co are slowly attacked.

Sb is dissolved with difficulty in concentrated HCl.

3. H₂SO₄, dilute, dissolves the same metals given above (excepting Sn), with the evolution of Hydrogen gas.

H₂SO₄, concentrated, hot, dissolves Ag, Cu, Bi, Hg and heavy metals generally with the evolution of SO₂ gas.

The metals easily dissolved by dilute H₂SO₄ are, as a rule, unaffected by cold concentrated H₂SO₄. Boiled with concentrated H₂SO₄, they are dissolved with the evolution of SO₂ gas.

4. A mixture of concentrated HCl and concentrated HNO₃, termed aqua regia, is the solvent for gold and platinum. They dissolve forming chlorides.

TABLE OF SOLUBILITIES.

	Acetate.	Arsenate.	Arsenite.	Borate.	Bromide.	Carbonate.	Chlorate.	Chloride.	Chromate.	Cyanide.	Fluoride.	Iodide.	Nitrate.	Oxalate.	Oxide.	Phosphate.	Silicate.	Sulphate.	Sulphide.	Tartrate.	Chloro- Platinates.	
Ag	a	a	a	a	a	a	a	a	a	a	a	a	a	a	a	a	b	ab	b	b	.	
Pb	ab	b	b	b	ab	q	a	c	ab	q	ab	b	a	b	b	q	b	c	ab	b	ab	.
Hg ₂ II.	a	b	b	b	bc	q	a	c	a	q	b	a	a	b	b	q	b	a	a	b	b	.
Hg II.	a	b	b	b	q	q	a	a	a	a	a	a	a	b	b	q	b	a	a	b	b	.
Bi	a	b	b	b	ab	q	a	a	a	q	a	a	a	b	b	q	b	a	a	b	b	.
Cu	a	b	b	b	q	q	a	a	a	q	a	a	a	b	b	q	b	a	a	b	b	.
Cd	a	b	b	ab	q	q	a	a	a	q	ab	a	a	b	b	q	b	a	a	b	ab	.
Sn II.	a	b	b	q	a	q	a	a	a	q	a	a	a	b	b	q	b	a	a	b	b	.
Sn IV.	a	b	b	?	ab	q	a	a	a	q	a	a	a	b	b	q	b	a	a	b	ab	.
Sb	a	b	b	?	q	q	a	a	a	q	a	a	a	b	b	q	b	a	a	b	b	.
Fe II.	a	b	b	b	a	q	a	a	a	q	ab	a	a	b	b	q	b	a	ab	b	ab	.
Fe IV.	a	b	b	b	a	q	a	a	a	q	a	a	a	b	b	q	b	a	a	b	a	.
Al	a	b	b	b	a	q	a	a	a	q	a	a	a	ab	b	q	bc	a	b	b	a	.
Cr	a	b	b	b	a	q	a	a	a	b	a	a	a	ab	b	b	b	a	b	b	a	.
Mn	a	b	b	b	a	q	a	a	a	b	a	a	a	ab	b	b	q	a	b	b	a	.
Zn	a	b	b	b	a	q	a	a	a	b	a	a	a	ab	b	b	q	a	b	b	a	.
Ni	a	b	b	b	a	q	a	a	a	q	ab	a	a	b	b	q	b	a	b	b	b	.
Co	a	b	b	b	a	q	a	a	a	bc	ab	a	a	b	b	q	b	a	b	b	b	.
Ba	a	b	b	b	a	q	a	a	a	b	bc	a	a	b	b	q	b	c	a	a	b	.
Sr	a	b	b	b	a	q	a	a	a	ab	bc	a	a	b	b	q	b	c	a	a	b	.
Ca	a	b	b	b	a	q	a	a	a	ab	bc	a	a	b	b	q	b	c	a	a	b	.
Mg	a	b	b	ab	a	q	a	a	a	a	bc	a	a	b	b	q	b	ab	a	b	ab	.
K	a	a	a	a	a	a	a	a	a	a	a	a	a	a	a	a	.	a	a	a	a	.
Na	a	a	a	a	a	a	a	a	a	a	a	a	a	a	a	a	.	a	a	a	a	.
NH ₄	a	a	a	a	a	a	a	a	a	a	a	a	a	a	a	a	.	a	a	a	a	.

a=soluble in water.
b=soluble in acids.
c=insoluble in acids.
ab=sparingly soluble in water.
bc=sparingly soluble in acids.

a = soluble in water.
 b = soluble in acids.
 c = insoluble in acids.
 ab = sparingly soluble in water.
 bc = sparingly soluble in acids.

Note. — For more complete information on the solubilities, refer to the preliminary reactions given on the metals and on the acids.

A. Treatment of a Solid (*not a Metal or Alloy*).

(a) Extract all substances soluble in boiling water.

Ascertain the reaction of this solution with litmus paper. Analyze a portion of the solution for the bases, in the usual manner.

According to the bases found to be present, examine the remainder of the solution for the acids which can be present. (See Table of Solubilities.)

(b) From the residue from (a), extract all substances soluble in HCl, dilute and concentrated, hot and cold.

Analyze a portion of this solution for the bases in the usual manner.

Ascertain what acids can be present (see Table of Solubilities) and examine the remainder of the solution for these.

(c) From the residue from (b), extract all substances soluble in HNO_3 , dilute and concentrated, hot and cold.

Analyze a portion of this solution for the bases in the usual manner.

Ascertain what acids can be present (see Table of Solubilities) and examine the remainder of the solution for these.

(d) From the residue from (c), extract all substances soluble in aqua regia (3 parts concentrated HCl, + 1 part concentrated HNO_3). Proceed as before.

(e) From the residue from (d), extract all substances soluble in NH_4OH . Examine for silver salts.

(f) From the residue from (e), extract all substances soluble in KOH or NaOH.

Examine for Pb or Sn compounds.

(g) Fuse residue from (f) + NaKCO_3 in iron crucible. Extract with water and examine solution for silicates and sulphate. Residue heat + $\text{HC}_2\text{H}_3\text{O}_2$. Solution. Examine for Ba + Sr. Residue fuse + KHSO_4 on Pt. Dissolve in water and examine solution for Fe, Al, Cr.

B. Treatment of a Solid (*a Metal or Alloy*).

Reduce the alloy to small fragments.

Place in a porcelain dish and warm + concentrated HNO_3 (use not more than 1 gram of the alloy).

Repeat the treatment with acid, if necessary, until no metallic particles remain. Evaporate to dryness. Add water containing a little HNO_3 , filter, wash.

Residue: Oxides of Sb and Sn heat + hot concentrated $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$. Solution. Examine for Sb by 64. If residue remains, examine for Sn by fusing + Na_2CO_3 + S, extracting Na_2SnS_3 with water, and examining solution for Sn by 58.

Examine the HNO_3 solution from the residue of Sb and Sn oxides for first, second, and third groups. (Fourth and fifth group metals are rarely found in alloys.)

NOTE (1).—If Au and Pt are present, they will be found with the residue of Sb and Sn oxides, as they are insoluble in HNO_3 . Suspend the residue in a little water, add bromine water, and warm gently. When the Au and Pt are dissolved, filter. Examine the residue for Sb and Sn as before. Divide the filtrate into two portions. Boil out excess of bromine. Examine one portion for Au by precipitation with FeSO_4 or oxalic acid. Examine the other portion for Pt by addition KBr. Evaporate and add alcohol. Precipitate = K_2PtBr_6 .

NOTE (2).—If the alloy contains phosphorus, it will be found in the residue from the HNO_3 treatment, combined as stannic phosphate. The fusion with the Na_2CO_3 + S will give Na_2SnS_3 and Na_3PO_4 . On acidifying this with acid, SnS_2 will be precipitated and the solution will contain H_3PO_4 . Examine this solution for phosphoric acid. (See 191.)

Questions in Qualitative Analysis.

1. A solution having an alkaline reaction is precipitated with dilute HCl. What may the precipitate contain? How would the ordinary course of analysis be modified?
2. What would be the effect of precipitating the metals with H_2S , without removal of the first group with HCl? Give a scheme for the separation of the precipitate obtained.
3. AgI and Ag_3PO_4 are both yellow. How would you distinguish between them? PbI_2 and PbCrO_4 ?
4. A precipitate consisting of a mixture of AgCl , PbCl_2 and Hg_2Cl_2 is exhausted with NH_4OH . The insoluble residue is treated with boiling H_2O , but no lead can be detected in the solution. Why?
5. Given a solution containing arsenious and arsenic compounds, how would you detect each? likewise in a solution containing stannous and stannic compounds, how would each be detected?
6. Explain the action of the following reducing agents: Nascent hydrogen, hydrogen gas + heat, H_2S , SO_2 , C, Fe. Give examples.
7. Explain the action of the following oxidizing agents, stating the conditions under which they are used: HNO_3 , Cl, Br, I, KNO_3 , KClO_3 , KClO , $\text{K}_2\text{Mn}_2\text{O}_8$, $\text{K}_2\text{Cr}_2\text{O}_7$. Give examples.
8. Convert a stannous into a stannic salt, by the use of yellow ammonium sulphide, and explain the action.

9. Two yellow solutions which contain no HNO_3 are treated with H_2S , sulphur separates in each case.

(a) The solution becomes colorless.

(b) The solution becomes green.

What are your inferences? Proofs?

10. A solution has not been made acid with HCl before the precipitation by H_2S . At the moment of the introduction of the H_2S , a white precipitate appears. What may it be?

11. What would be the effect of an excessive amount of HCl , HNO_3 or H_2SO_4 before the addition of H_2S ? How could these undesirable conditions be rectified?

12. What would be the effect of allowing the precipitated sulphides of the second group to stand some time before analysis; of washing them with pure water?

13. A solution made by mixing aqueous solutions of the chlorides of the metals, contains a white precipitate. What may it be? Prove it.

14. A mixture of the sulphides of the second group is treated with concentrated HNO_3 . An insoluble residue remains. What may it contain? Analyze it.

15. After Pb had been removed in the second group with H_2SO_4 , NH_4OH was added. The white flocculent precipitate obtained was dissolved in HCl and water added. No precipitate was obtained. Why?

16. In the separation of As_2S_3 , Sb_2S_3 , SnS_2 , with concentrated HCl , why cannot a portion of the solution be examined directly for Sn by adding HgCl_2 instead of using the method given?

17. Account for the occurrence of Pb in different parts of the scheme of analysis.

18. If Cd is not completely removed in the second group, where will it be found? Why? How can its presence be proved? Under what conditions is Cd not removed in the second group?
19. A solution containing Fe (ferric), Al, Cr, Mn, Zn, Ni, Co salts, is treated with $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$. What is the precipitate obtained? Analyze it. Use KOH instead of $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$. What is the result?

If an insufficient quantity of NH_4Cl were added, what would be the result?

What would be the effect if, after the addition of the NH_4OH and NH_4Cl , the whole were allowed to stand before analysis?

20. The third group precipitate is washed with pure water; what is the effect?
21. What would be the effect of allowing the precipitated sulphides of the third group to stand some time before analysis?
22. Which is preferable for the precipitation of the third group, colorless or yellow ammonium sulphide? Why?
23. In separating the precipitate containing the third group, with HCl, what would be the effect if the filtrate were not boiled to expel the H_2S ?
24. When the residue consisting of $\text{Fe}_2(\text{OH})_6$ and $\text{Mn}_2\text{O}_3(\text{OH})_2$ is dissolved in HCl, why is Cl given off, and why is it boiled out? What would be the effect if it were not boiled out?
25. What would be the result if a solution containing phosphates and oxalates were analyzed by the regular scheme of analysis instead of by the special scheme? Do these acids interfere with the analysis of the first and second groups?

26. Take a solution containing the members of the first, second and third groups. First add NH_4OH to alkaline reaction. Second, add it in excess. State the effect in each case. Use KOH similarly. What is the effect in each case?
27. Why is the precipitation of the fourth group with $(\text{NH}_4)_2\text{C}_2\text{O}_4$ to be preferred to that by $(\text{NH}_4)_2\text{CO}_3$?
28. Why must this precipitate be ignited before proceeding with the analysis?
29. What would be the effect of a solution of CaSO_4 on a solution of BaCl_2 ?
 SrCl_2 ?
 CaCl_2 ?
30. Given a solution containing BaCl_2 , SrCl_2 , CaCl_2 . Analyze it with the use of $\text{C}_2\text{H}_5\text{OH}$.
31. Why is magnesium found in the fifth group and not in the fourth?
32. Why are NH_4 compounds tested for in the original solution and not in the fifth group?
33. An acid solution containing ammonium salts was treated with NaOH and boiled, but no odor of NH_3 was developed. Why?
34. What would be the effect of incomplete precipitation and incomplete washing of precipitates?
35. If the members of the various groups are incompletely precipitated by the group reagents, state where each member, so lost, will be found in the course of the regular scheme of analysis used.
36. What is the action of HNO_3 on metals generally? What is the action of aqua regia? How do the products resulting from the action of HNO_3 differ

from those resulting from the action of aqua regia? Why does aqua regia dissolve Au and Pt while HCl or HNO_3 does not?

37. Red oxide of lead is not dissolved by water nor HNO_3 , but on the addition of a small quantity of solution of KNO_2 or $\text{H}_2\text{C}_2\text{O}_4$ to the HNO_3 it is dissolved. Explain the action.
38. Fe_2O_3 , Cr_2O_3 , Al_2O_3 , after ignition at a high heat, are practically insoluble in acids. Given the following fluxes:
 Na_2CO_3 , KNO_3 , KHSO_4 , NaBO_2 ,
 How could these oxides be brought into solution? State reasons.
39. Describe several ways of proving whether a powder under examination is an oxide.
 State in what cases each method can be used. Give examples.
40. A powder given for analysis evolves oxygen on being heated. Does this fact necessarily demonstrate the presence of certain oxides? Draw up a list of the substances that yield oxygen on being heated.
41. On treating a powder with HCl and heating, Cl is evolved. Give a list of the substances which would cause this.
42. A dry substance is heated in a glass tube closed at one end.
 - (a) Liquid condenses in the cool part.
 1. It is neutral.
 2. It is alkaline.
 3. It is acid.
 - (b) Gases or fumes are given off.
 1. O is evolved.
 2. CO_2 is evolved.
 3. NO_2 is evolved.

(c) Sublimate is formed.

1. Hg.

2. S.

(d) Residue blackens.

State what substances are indicated by each result.

43. A powder submitted for analysis was:—

1. Heated on charcoal with Na_2CO_3 in reducing and oxidizing flames.

2. Heated on charcoal with $\text{Co}(\text{NO}_3)_2$.

3. Borax and microcosmic salt beads were made with it.

4. HCl and Pt wire (flame test).

Give all deductions.

44. A solution containing no acetic acid, but a quantity of $\text{K}_2\text{Cr}_2\text{O}_7$, or some other oxidizing agent, gives, on testing for acetic acid by means $\text{C}_2\text{H}_5\text{OH}$ and H_2SO_4 , a peculiar odor. To what is it due?

45. In examining for H_3AsO_4 by (a), analysis of the acids, why is the precipitate obtained still further tested for arsenic? Why is not the formation of this precipitate sufficient evidence?

46. Could a yellow precipitate formed in testing for H_3AsO_3 in (b) be sulphur? Why not?

47. A solution containing Cu was tested for boric acid by 155. Was the test conclusive? Would you suggest a modification?

48. Under what conditions is it necessary to test a solution having an acid reaction for carbonates?

49. A solution was found to contain sulphides. It was subsequently tested for chromic acid. Was it found? State reasons.

50. Under what conditions does silver nitrate fail to precipitate Cl, Br, and I from compounds containing them?
51. How would you determine the presence of HCl, HBr, and HI in the cases of one, two, or all three of these acids being present? State reasons.
52. Given a solution containing free bromine and iodine, how could this solution be examined for HBr and HI?
53. Explain how the formation of Prussian blue in 171 is an evidence of HCN.
54. Is it rational to examine for HF, in solutions kept in glass vessels? Why?
55. Under what conditions may a solution contain sulphides? What would be the reaction of this solution toward litmus paper?
What metals could be found in a solution containing sulphides?
56. How could a solution or a substance containing sulphides and sulphates be examined for each?
57. Is it necessary to examine a substance which is insoluble in water for the presence of nitrates?
58. Oxalates and carbonates when treated with concentrated H_2SO_4 both yield CO_2 . How can you distinguish between these acids by this test?
59. Under what conditions would you examine a neutral aqueous solution for phosphates?
60. An insoluble silicate is fused with KHSO_4 and the fused mass is extracted with water. Where will the silica be found? Why?

61. A solution which is acid with HCl , is treated with BaCl_2 . Is the white precipitate produced necessarily a sure indication of H_2SO_4 ?
62. In what case may BaSO_4 be found in a solution?
63. The residue left on the evaporation of a solution containing no carbonates, shows carbonates after ignition. To what may this be due?

